UDC 666.52

COMPOSITION AND PROPERTIES OF SOFT PORCELAIN

A. P. Zubekhin,[1] S. P. Golovanova,[1] A. S. Deeva,[1] and N. D. Yatsenko[1]

Translated from *Steklo i Keramika*, No. 6, pp. 22 – 24, June, 2009.

The possibility of obtaining soft porcelain from ceramic pastes based on unenriched kaolin from the Donetsk deposit is examined. The physical – mechanical properties and whiteness of the samples obtained are determined. The dependence of the coefficient of reflection of individual phases of porcelain on the Fe_2O_3 content is investigated.

Key words: soft porcelain, unenriched kaolin, mullite, glass phase, coefficient of reflection.

The most important conditions for manufacturing competitive products, at the present time, are high technical-performance and aesthetic characteristics. In the production of ceramic articles, specifically, porcelain, the most stringent requirements are imposed on its whiteness. The whiteness and chromaticity of porcelain depend on the presence of coloring impurities, the main ones being iron and titanium oxides and compounds present in many natural raw materials, including in kaolins and white-burning clays [1 – 3].

Soft porcelain is one of the effective and competitive materials for the production of household and art objects. However, it is not used much for manufacturing household objects because its technology is still underdeveloped. To obtain competitive soft, as opposed to hard, porcelain it is important to develop a resource-conserving technology based on different raw materials which give low firing temperatures and high technical and aesthetic performance characteristics.

The following raw materials were used to develop a composition for soft porcelain: kaolin from the Prosyanovskoe deposit, high-plasticity white-burning clay from the Vladimirovskoe deposit (Rostov Oblast'), and pegmatite and feldspar from the Chupinskoe deposit. The possibility of using unenriched kaolin from the Donetskoe deposit (Ukraine) was studied because Prosyanovskoe kaolin is in short supply and expensive. The chemical properties of these materials are presented in Table 1.

The following ceramic paste is recommended in [1, 2] for obtaining soft porcelain at lower firing temperatures (%[2]): 60 – 70 SiO_2, 25 – 35 Al_2O_3, and at least 5 R_2O. Taking this composition as a base, we researched the possibility of developing ceramic pastes for soft porcelain using Prosyanov kaolin (composition 1-P) as well as partial substitution of unenriched Donetskoe kaolin (compositions 1-D – 5-D). The chemical compositions of the ceramic pastes are presented in Table 2.

To determine the optimal firing temperatures and compositions of soft porcelain based on Donetskoe kaolin and to compare with the composition 1-P, samples were fired in a laboratory electric furnace at temperatures 1150 and 1200°C with isothermal soaking for 1 h.

[1] South-Russia State Technical University, Novocherkassk, Russia.

[2] Here and below, the content by weight.

TABLE 1.

Material	Content, wt.%								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	clacination losses
Kaolin:									
Prosyanovskoe	48.90	36.45	0.68	0.24	–	1.01	0.82	0.45	12.40
Donetskoe	69.53	17.10	0.40	0.30	0.56	0.40	11.30		0.21
Vladimirovskoe clay	55.48	22.21	1.96	0.65	0.83	1.39	2.64	0.82	9.51
Chupinskoe feldspar	63.13	21.27	0.30	–	0.83	0.50	12.04	1.62	0.31
Chupinskoe pegmatite	77.69	15.22	0.40	–	1.34	1.03	4.23	3.24	0.09

TABLE 2.

Composition	Content, wt.%							
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	$K_2O + Na_2O$	calcination losses
1-P	63.61	23.56	0.65	0.18	0.75	0.84	5.51	4.70
1-D	63.35	23.08	0.54	0.29	0.63	0.69	7.46	3.95
2-D	64.45	22.11	0.55	0.33	0.63	0.64	7.87	3.42
3-D	64.71	22.18	0.61	0.41	0.65	0.66	6.98	3.79
4-D	64.63	21.85	0.58	0.41	0.62	0.58	8.12	3.20
5-D	65.77	21.24	0.59	0.41	0.68	0.63	7.49	3.18

The physical-mechanical properties and whiteness of the fired samples were determined. The whiteness of the samples, which is characterized by the coefficient of reflection (CR), was determined with a FM-56 photometer using a reference standard — MS-20 matte glass with CR = 96.6%.

It was determined that the 1-D – 5-D samples of soft porcelain fired at 1150°C meet the water absorption, density, and fire shrinkage requirements established for such articles (Table 3). The CR of these samples is 72 – 76%, which is higher than the CR of samples 1-P, obtained with Prosyanovskoe kaolin. The physical – mechanical properties of the samples 1-P fired at the same temperature do not satisfy the standards for soft porcelain. These samples are characterized by high porosity and water absorption and low firing shrinkage.

The physical – mechanical properties of soft porcelain made with Prosyanovskoe kaolin and with unenriched Donetskoe kaolin fired at 1200°C meet the requirements for soft porcelain. The whiteness of porcelain does not change in the same way: for the samples 2-D – 5-D the coefficient of reflection is lower than for the samples obtained at 1150°C.

TABLE 3.

Composition	Firing shrinkage, %	Water absorption, %	Density, kg/m^3	Porosity, %	CR, %
Firing temperature 1150°C					
1-P	7.20	8.50	1230	28.30	74
1-D	14.20	0.05	2295	0.12	76
2-D	12.07	0.06	2190	0.12	74
3-D	13.40	0.16	2266	0.25	73
4-D	7.95	0.13	2150	0.28	72
5-D	10.00	0.11	2100	0.25	72
Firing temperature 1200°C					
1-P	10.28	0.10	2230	0.23	72
1-D	12.70	0.001	2005	0.08	76
2-D	10.70	0.05	2040	0.10	72
3-D	11.50	0.07	2050	0.10	71
4-D	7.04	0.09	1990	0.17	69
5-D	9.10	0.06	2125	0.12	65

In summary, the optimal firing temperature of soft porcelain based on ceramic pastes formed with unenriched Donetskoe kaolin substituting for 30 – 45% Prosyanovskoe kaolin is 1150°C.

X-ray diffraction analysis of the samples (DRON-3 diffractometer) showed that the main phases of soft porcelain are mullite, quartz, and cristoballite as well as a substantial amount of a glass phase (see Fig. 1). A fayalite phase, which many investigators claim can form, was not found.

To determine the mechanism by which iron oxides affect the whiteness of porcelain, it is important to study the dependence of the CR of the individual phases on the Fe_2O_3 content. We studied the effect of Fe_2O_3 in amounts 0.5, 1.0, and 3.0% on the main phases of porcelain: mullite and glass (Table 4).

All samples with Fe_2O_3 additions were obtained by sintering at 1450°C with isothermal soaking for up to 14 h followed by cooling in air. After comminution to the same degree of fineness as determined from the specific surface area (300 m^2/kg), x-ray diffraction was used to determine their phase composition and the CR was determined.

The CR of the porcelain phases presented above, all having the same Fe_2O_3 content, does not vary in the same way. For example, the CR of mullite containing 0.5% Fe_2O_3 decreases only by 3.8%; but when the amount of Fe_2O_3 increases to 1% the CR changes by 9.7% as compared with an iron-free sample. As the Fe_2O_3 content increases (3%), the CR decreases by 18.8%. A change of a different character in the CR is observed in the glass phase of soft porcelain: the CR decreases by 7.07% even for 0.5% Fe_2O_3 while for 3%

TABLE 4.

Fe_2O_3 content in porcelain, wt.%	Whiteness (CR) of porcelain phases, %	
	mullite	glass*
–	92.80	86.12
0.5	89.00	79.09
1.0	83.10	70.90
3.0	74.00	48.30

* Glass content (wt.%): 76 SiO_2, 15 Al_2O_3, 9 K_2O.

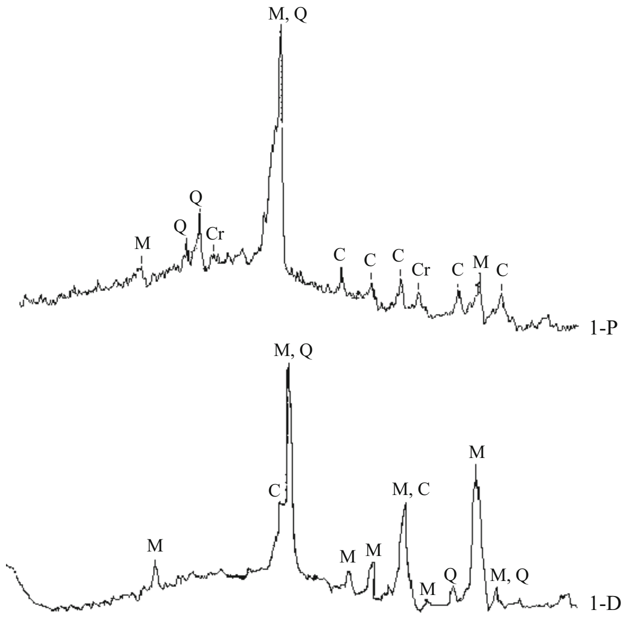

Fig. 1. X-ray diffraction pattern of soft porcelain with the compositions 1-P and 1-D: M) mullite; Q) quartz; Cr) cristoballite; C) corundum.

Fe_2O_3 the CR decreases by 37.82%. In our opinion, this is because the mechanism of isomorphic substitution of Fe^{3+} ions for Al^{3+} ions in mullite is different and the distribution of Fe ions in the glass network is different.

When $[AlO_4]^{4-}$ tetrahedra and $[AlO_6]^{9-}$ octahedra are present in the crystal lattice of mullite, isomorphic substitutions of Fe^{3+} ions, which likewise can be in the form of $[FeO_4]^{5-}$ tetrahedra and $[FeO_6]^{9-}$ octahedra, can occur; substitutions of groupings of the same type are most likely to occur: $[AlO_6]^{9-} \rightarrow [FeO_6]^{9-}$. These isovalent substitutions of Al^{3+} and Fe^{3+} ions, whose crystal-chemical parameters are all close, do not bring about any substantial changes of the electronic and crystalline structure of mullite, so that strong light absorption does not occur, i.e., the CR does not decrease.

In the glass network of porcelain, the Al ions are found only in the form of $[AlO_4]^{4-}$ tetrahedra; substitution of the equivalent tetrahedron $[FeO_4]^{5-}$ makes it necessary to compensate the extra electron by means of a univalent Na^+ or K^+ ion [4]. This is accompanied by definite crystal-chemical changes in the glass network, which increase light absorption, i.e., decrease the CR.

The results obtained in the present work have revealed the mechanism by which iron oxide affects the mullite crystalline phase and the glass phase, which are well known to predetermine the properties of porcelain.

In summary, it has be shown that in the production of soft porcelain a portion of the Prosyanovskoe kaolin can be replaced with less expensive and more accessible kaolin from the Donetsk deposit.

REFERENCES

1. A. I. Avgustinik, *Ceramics* [in Russian], Stroiizdat, Leningrad (1975).
2. A. A. Krupa and V. S. Gorodov, *Chemical Technology of Ceramic Materials* [in Russian], Vishcha shkola, Kiev (1990).
3. I. Ya. Guzman (ed.), *Chemical Technology of Ceramics* [in Russian], Stroimaterialy JSC, Moscow (2003).
4. N. M. Pavlushkin (ed.), *Chemical Technology of Glass and Sitals* [in Russian], Stroiizdat, Moscow (1983).